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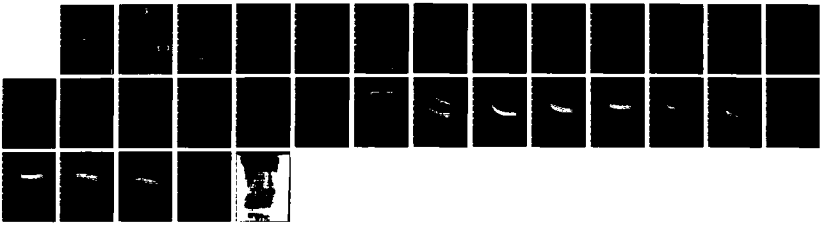

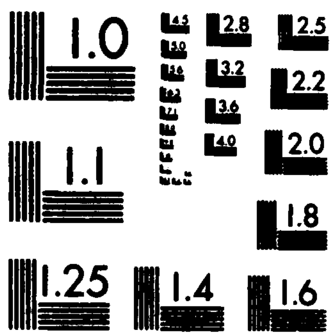

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REPORT NO. NADC-82227-60

NATURAL WEATHERING OF SELECTED ORGANIC MATRIX COMPOSITES

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Natural Weathering	Aircraft Carrier
Mechanical Properties	Degradation
Moisture	Paint Coating

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A study was made of selected graphite organic matrix composite materials exposed to natural weathering at Panama and Warminster.

Commercially available composite prepregs were fabricated into panels using principally a 8 ply layup ($\pm 45^{o}$) and a 16 ply layup (0^{o} $\pm 45^{o}$ 90^{o}). Panels were retrieved periodically and mechanical property determinations were made at room temperature, 82.2°C (180°F) and 121.1°C (250°F). Tension,

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) flexure, compression, short beam shear and in-plane shear tests were primarily used to assess the damage.

At room temperature, the in-plane shear strength property of the $\pm 45^{\circ}$ panels was unaffected by exposure. At elevated temperature, however, this matrix dominated property generally decreased with increasing exposure time.

Data indicated that the combination of moisture and elevated temperature caused a decrease in the matrix dominated mechanical properties of the 16 ply panels. Some graphite organic matrix composites degraded at a faster rate than others.

Panama exposed panels show a greater degradation in static strength at elevated temperatures than panels exposed at Warminster.

The use of a paint coating seemed to decrease the irreversible degradation due to moisture and ultraviolet irradiation.

A one time exp[illegible] aboard different aircraft carriers was made of one of the graphite/epoxy composite systems. The static mechanical properties of the exposed panels were also degraded at the elevated temperature.

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INTRODUCTION

Composite materials are being increasingly utilized in Naval aircraft structures. These stiff, strong, lightweight materials have been successfully applied to various types of secondary structure and are currently being applied to primary structure. Composites, however are inhomogenous anisotropic materials which have different defect and damage characteristics from those of the traditional metallic structural materials. A number of different reinforcements have been successfully utilized in composite systems. Fiberglass has been used extensively in polyester and epoxy resin composites. Presently, graphite and Kevlar epoxy systems (GR/EP and K/EP) are being utilized to an increasing extent in aircraft composite airframe construction. Those designs employing graphite have ranged from thick skinned strain limited construction to thin skins over honeycomb in a stiffness limited application.

Present day GR/EP systems were originally represented as 177°C (350°F) service materials. Increasing evidence disclosed various factors which precluded consideration of these resins for airframe applications in excess of 121.1°C.[1, 2, 3] The factor which had received the most attention has been moisture. It is well established that moisture plasticizes the resin matrix at elevated temperatures. The properties affected are those that are matrix or resin dependent such as shear or compression. This effect is reversible if the composite is heated to allow moisture effusion. In a sound laminate the moisture diffusion and distribution would be expected to follow classic Fickian predictions. Very thick laminates, greater than 40 plies, take a relatively long time to reach equilibrium saturation levels of absorbed moisture. The state-of-the-art 177°C curing epoxies such as Hercules AS/3501 and Celanese T300/5208 absorb approximately 1.6% moisture at 95% R.H. and 60°C (140°F). These levels are for unpainted panels. Coating the laminates with epoxy polyamide primer and polyurethane topcoat results in higher moisture saturation levels.

There are other environmental factors, such as ultraviolet radiation, which can have a deleterious effect on organic matrix composites. Ultraviolet radiation can lead to deterioration in organics.[4] The amount of degradation is dependent on the intensity and duration of the exposure. Graphite acts as a ultraviolet absorber thereby mitigating to some degree the extent of damage. Coating completely precludes ultraviolet damage of GR/EP composites. Thin laminates would be expected to be degraded to a greater extent than thick ones because of the greater percentage of the total thickness being affected.

This study was undertaken to determine the real time effects of natural exposure at various sites on specific graphite reinforced organic matrix composites. The sites of exposure were: Warminster, Pennsylvania and Panama, the Atlantic Ocean side. Residual mechanical properties were determined as a function of exposure at a particular site.

Results show the effects of natural environments on commercially available organic composites. This effort is an engineering study directed at establishing a basis for comparison of composites under specific environmental exposure conditions.

EXPERIMENTAL PROCEDURE

Commercially available composite prepregs were fabricated, cured in an autoclave, cut into panels, exposed to natural weathering in Panama and Warminster, Pennsylvania, periodically retrieved and mechanical property determintions made at R.T. 82.2°C and 121.1°C. Tension, flexure, compression, short beam shear and in-plane shear tests were primarily used to assess the effects of exposure.

1. Fabrication

The commercial prepreg materials included in this study are presented in Table I. Eight ply panels (± 45) 6 inches by 9 inches, were manufactured for the 300, 800, 900 and 1000 series. The 400 series, 10 ply laminates, consisted of 0° ± 45 orientation with the 0° ply fabricated on the outside. Sixteen ply panels, (0 ± 45 90) 8 inches by 9-1/2 inches, were made for the 800, 900 and 1000 series.

Within each series, half of the panels were coated with an epoxy polyamide primer (MIL-C-23377C) followed by a polyurethane (MIL-C-81773B, AS) topcoat for a total thickness of approximately 5 mils. The remaining half of the panels were uncoated.

2. Natural Weathering Sites

The average environmental parameters of the Panama[4] and Warminister sites are presented in Table II.

Retrievals were made periodically, approximately at 6 month intervals.

The 300 and 400 series were initiated in January 1977 and the 800, 900 and 1000 series one year later in 1978.

A one time exposure aboard two different aircraft carriers was made of the AS/3501-6 graphite epoxy system. The panels were exposed for 10 months on the NIMITZ, a nuclear carrier and for 8 months on the U.S. CONSTELLATION, both operating in the Pacific theater.

3. Physical and Mechanical Tests

The tensile specimens were straight sided 1 inch by 9 inch and were tested to failure.

Flexure specimens, 1/2 inch by 2-7/8 inches were tested to failure in 3 point bending. Compression specimens, 3/4 inch by 6-1/2 inches, were supported by horizontal tabs to prevent buckling and were tested using a modified Illinois Institute of Technology Research Institute compression test fixture. Short beam shear specimens, 0.25 inches by 0.5 inches, were tested to failure in 3 point bending.

The 6 inch by 9 inch panels, were cut into five tensile specimens. The 0^{o} tensile strength (in-plane shear) of these $\pm$ 45^{o} panels was measured at R.T., 82.2^{o}C and 121.1^{o}C. Two of the 5 tensile specimens tested at R.T. had biaxial strain gages bonded to them in order to determine Poisson's ratio, modulus and strain to failure.

The 8 inch by 9-1/2 inch (0 $\pm$ 45 90) panels were cut into three tensile (one was strain gaged) and compression specimens, and five flexure and short beam shear specimens.

In addition to the mechanical property determinations, weight measurements were made on each panel before and after exposure to determine the percent increase in moisture. Panels retrieved from Panama were sealed in vapor barrier proof bags prior to returning to Warminster.

Visual examinations were performed on all exposed panels. Micro-examination and Scanning Electron Microscopy (SEM) were performed on specific specimens.

All data were routinely examined for indications of significant trends. Standard deviations and coefficient of variations were determined for specimen replicates.

RESULTS AND DISCUSSION

At room temperature the in-plane shear strength property of the ± 45° panels was unaffected by exposure. At elevated temperature, however, this matrix dominated property generally decreased with increasing time.

The fiber controlled property of the 16 ply (0 ± 45 90) laminates, 0° tension, was basically unaffected by the combination of moisture and elevated temperature. The matrix controlled properties such as shear and flexure, however, were significantly affected. The strength decreases as exposure time increases and the rate of decrease varies with each graphite/matrix system.

In general, the Panama exposed panels showed a slightly greater degradation in static strength at elevated temperature than Warminster exposed panels

Each graphite/matrix system will be addressed separately and representative data will be presented.

AS/3501-6 (300, 400, 900 Series)

300 Series, 8 Ply (± 45)

The trend of data for increasing exposure time is shown in Figure 1. The in-plane shear strength decreases as exposure time increases for specimens tested at elevated temperature. The rate of decrease levels off between 18 to 24 months exposure. Room temperature and 82.2°C temperature tests show no adverse affects of outdoor weathering. The increased strength retained at room temperature and 82.2°C evidence post aging behavior that is less marked at the latter temperature.

Warminster exposed panels show approximately the same behavior but to a somewhat lesser degree.

400 Series 10 Ply (0 ± 45)

The effect of moisture and temperature on resin dependent properties such as shear is shown in Figure 2. The unpainted panels, tested at room temperature are unaffected by Warminster exposure. At elevated temperatures, however, the coated panels show a degradation effect that is particularly marked at 121.1°C. The 1 to 12 months test data decreases at a faster rate than those tested after one year of exposure. Tests results at elevated temperature show some overlapping with regard to the percentage of retained strength.

Flexure test data shows an increase in residual strength at room temperature. Elevated temperature tests show a very gradual decrease at 82.2°C to a 85% retention of residual strength after three years;at 121.1°C the loss of strength is closer to 20%.

900 Series, 16 Ply (0 $\pm$ 45 90) and 8 Ply ($\pm$ 45)

The trend of the 900 series data for the in-plane shear strength of the $\pm$ 45 panels is similar to the data presented for the 300 series. The room temperature in-plane shear strength is unaffected by exposure. At elevated temperature, the in-plane shear degradation increases with increasing exposure time, especially during the first year. When tested at 121.1°C the Panama exposed panels decrease at a faster rate than the Warminster exposed panels, Figures 3 and 4.

The strength of the fiber controlled property, 0° tension, of the 16 ply painted (0 $\pm$ 45 90) panels are slightly affected by both exposure (at Panama or Warminster) and test temperature, Figures 5 and 6.

The matrix controlled properties, however, are significantly affect[illegible] In particular the flexure strength of the Panama exposed panels, tested 121.1°C, lose as much as 30% of the residual strength, Figure 7. Warmir[illegible] r exposed panels, tested at 121.1°C do not show any degradation until afte[illegible] about 18 months of exposure and retain approximately 80% of the residual strength after 3 years of exposure.

The moisture content for the Panama exposed panels was approximately 1% after 3 years of exposure. The Warminster exposed panels contained somewhat less moisture for the same exposure time, about 0.7%. Figure 8 shows the moisture content as a function of time. These moisture contents are representative of the average trend of moisture data for the graphite/epoxy systems included in this study.

With long term exposures there might be a tendency to lose a slight amount of the coating or resin depending on whether the panel was coated or uncoated. This occurrence would tend to decrease weight with increasing exposure time.

Panels of the painted 16 ply (0 $\pm$ 45 90) AS/3501-6 were subjected to actual shipboard exposure in the Pacific theater. Aboard the NIMITZ, a nuclear carrier, the environmental exposure was primarly sea spray. The panels on the U. S. CONSTELLATION were exposed to sea spray and stack gases.

As shown in Table III, the combination of moisture and elevated temperature affected the matrix controlled shear and flexural strength. Percent reduction of the shear strength tested at 121.1°F and after 10 months exposure aboard the NIMITZ is close to 30%.

The greater degree of degradation in the NIMITZ exposure might be attributed in part to the longer time of exposure. A much more significant effect, however, would be the actual environmental conditions during the duration of the exposure. It is known[5] that seasonal variations in humidity can promote significant moisture content differences in GR/EP composites, particularly if the surface to edge area ratio is not great.

It is interesting to note that conventional carriers like the CONSTELLATION have SO_2 in the shipboard environment. This apparently did not have any significant effect on resin properties of the composite. This would correlate with previous work conducted by this laboratory showing a salt laden SO_2 environment to have negligible effect on GR/EP mechanical properties, excepting the influence of moisture.

AS/3004 (800 Series)

The 800 series, AS fiber with 3004, a polysulfone matrix, was the only graphite system included in this study that was prepregged with a resin other than an epoxy.

Because of a limited supply of specimens, some elevated temperature tests were eliminated. Panama exposed panels, 8 and 16 ply, were tested at room temperature and 121.1°C. The 8 ply Warminster exposed panels were tested at room temperature and 121.1°C; 16 ply panels were tested at 121.1°C only.

The flexure, shear and tensile strength data of the Panama and Warminster exposed panels did not show much effect of exposure.

The elevated temperature tests of the Warminster exposed panels are interesting in that the matrix shear property does not seem to be significantly affected. Figure 9 shows only a very slight affect on interlaminar shear strength after 3 years of exposure.

Figure 10 shows the elevated temperature tensile data as a function of exposure time in Warminster. Little change is evident in retained strength of this fiber dominated property. Panama exposures of this material exhibited similar behavior, reflecting little effect of exposure.

It is interesting to note that both matrix and fiber dominant properties seem to be relatively unchanged after 3 years of exposure. This material was found to exhibit much lower saturation values of moisture than the epoxies, about 0.3 wt. %. The small effect on interlaminar shear strength at elevated temperature indicates little moisture affect on this polymer. This apparent lack of moisture effect is in direct contrast to the behavior of the epoxy systems studied.

T300/5208 (1000 Series)

The mechanical properties of the T300/5208, 1000 series, showed less change with increasing exposure time than the AS/3501-6 system.

The in-plane shear strength of the matrix controlled $\pm 45^\circ$ Panama exposed panels was not greatly affected by exposure time or elevated temperature. As shown in Figure 11, better than 90% of the residual shear strength is retained after 18 months of Panama exposure when tested at 121.1°C.

The elevated temperature in-plane (± 45) shear strength of the T300/5208 material does not evidence the same degree of degradation as the AS/3501-6 (300, 400 and 900 series) epoxy system.

As shown in Figure 12, there is an apparent deterioration in the in-plane shear strength with an increasing exposure time at Warminster although the amount of reduction is not as much as evidenced with the other epoxy system. Since these reduced properties are those of coated materials this deterioration can be attributed to moisture.

Data for the 16 ply mechanical tests showed similar trends in that neither the fiber nor resin controlled properties were affected by exposure to the same degree as the AS/3501-6 epoxy system.

SUMMARY OF RESULTS

Three different organic matrix systems were exposed to natural weathering at two different exposure sites reflecting differing environmental conditions. The saturated coated GR/EP systems absorbed approximately 1% moisture after exposure in Panama and approximately 0.7% after Warminster exposure. The moisture laden epoxy systems showed degradation in the elevated temperature matrix dominant properties. The T300/5208 material degraded less than the AS-3501-6 material. Room temperature uncoated tensile and flexure strength were affected to some degree by a combination of ultraviolet radiation and moisture which is more of an erosive degradation. Carrier exposure of coated GR/EP correlates with Panama and Warminster site deterioration data and give evidence to the plasticizing effects of moisture on GR/EP.

The coated AS/polysulfone panels, at equilibrium, absorbed approximately 0.3% moisture in weight after Panama exposure. The elevated temperature matrix properties were affected less by exposure than the epoxy systems.

CONCLUSIONS

Generally, the 177°C curing epoxy sys ms exhibited sensitivity to moisture particularly in elevated temperature matrix dominant properties. The T300/5208 GR/EP system exhibited less degradation under these particular conditions than the AS/3501-6 material. The GR/EP systems absorbed considerably more moisture than the GR/polysulfone system.

The GR/polysulfone material appears to undergo very little property reductions due to absorbed moisture. Its elevated temperature matrix dominant properties were affected less by exposure than the epoxy system.

Carrier stack gas exposure does not appear to have much affect on the mechanical properties of GR/EP.

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(4) R. E. Trabocco, "Natural Exposure of Selected Graphite/Epoxy Composite Material Systems," NADC Report No. 80021-60 of 31 July 1980

(5) P. M. Stifel, "Carrier Testing OF Graphite Composites in Contact with Metals on F-4" NADC Report No. 76010-30

TABLE I

GRAPHITE/MATRIX SYSTEMS

Series	Fiber	Matrix - Type	No. of Plies	Ply Orientation
300	AS	3501-6 - Epoxy	8 ply	± 45 $(+45\ -45\ +45\ -45)_s$
400	AS	3501-6 - Epoxy	10 ply	$(0\ +45\ -45\ +45\ -45)_s$
800	AS	3004 - Polysulfone	8 ply 16 ply	± 45 $(+45\ 0\ -45\ 0\ +45\ 0\ -45\ 90)_s$
900	AS	3501-6 - Epoxy	8 ply 16 ply	$+45$ $(+45\ 0\ -45\ 0\ +45\ 0\ -45\ 90)_s$
1000	T300	5208 - Epoxy	8 ply 16 ply	± 45 $(+45\ 0\ -45\ 0\ +45\ 0\ -45\ 90)_s$

TABLE II

ENVIRONMENTAL PARAMETERS OF EXPOSURE SITES

	Fort Sherman (Canal Zone) (Coco Solo)	Naval Air Facility (Warminster, PA)
Precipitation, in.	130	40
Temperature, °F	86 to 87	43 to 61
Relative Humidity, %	82	63 to 90

TABLE III

RESULTS OF AS/3501-6 EXPOSURE ON U.S. CONSTELLATION (CVA) AND NIMITZ (CVN) CARRIERS

	Unpainted Unexposed	U.S. CONSTELLATION (CVA) Exposure	NIMITZ (CVN)* Exposure
Tensile Strength			
P.S.I.			
R.T.	55831	62922	58821
82.2°C	57432	61674	63292
121.1°C	61016	60111	57767
Shear Strength			
P.S.I.			
R.T.	6257	6149	6015
82.2°C	5964	6157	6807
121.1°C	6108	5920	4276
Flexural Strength			
P.S.I.			
R.T.	53232	52178	56489
82.2°C	52389	47253	59933
121.1°C	53544	46164	49191

*Nuclear Carrier

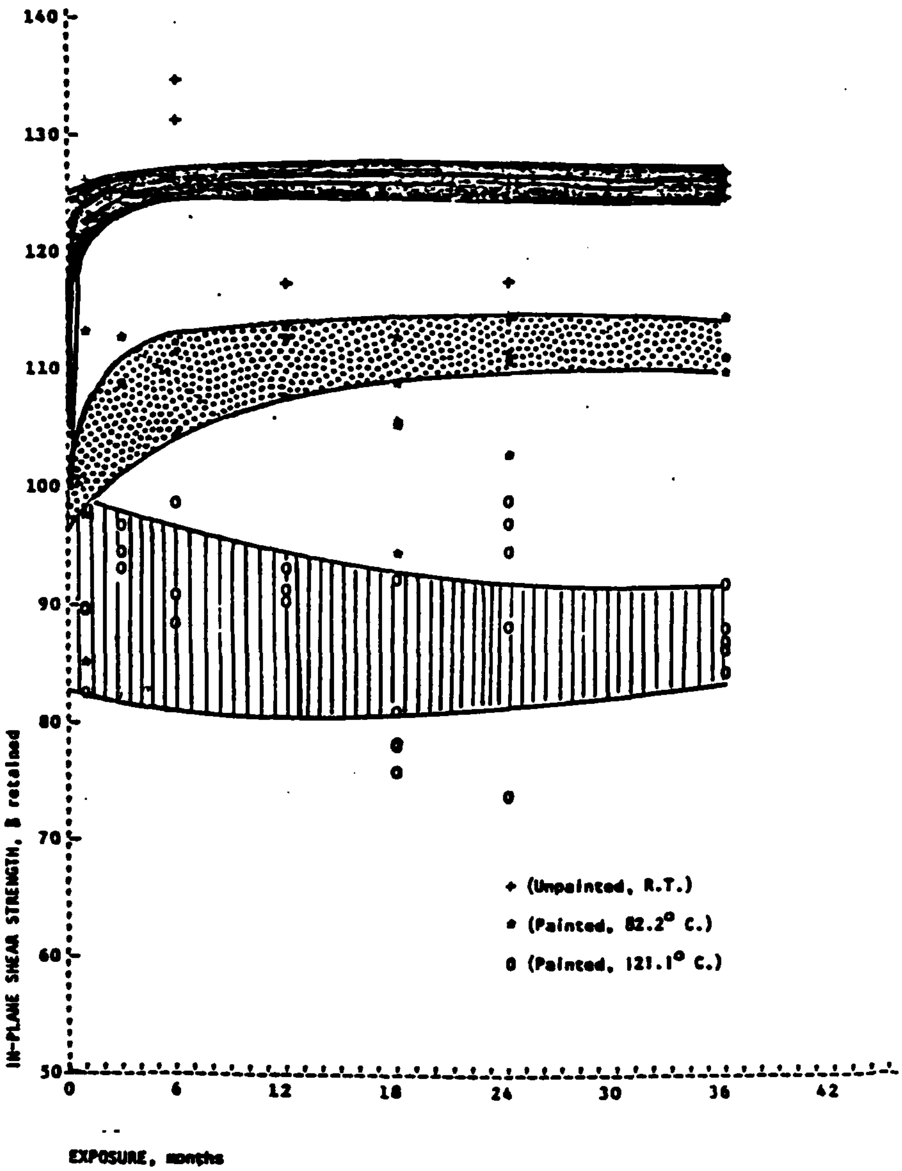

Figure 1. 300 Series, 8 Ply (± 45) Panama, % Retained In-Plane Shear Strength

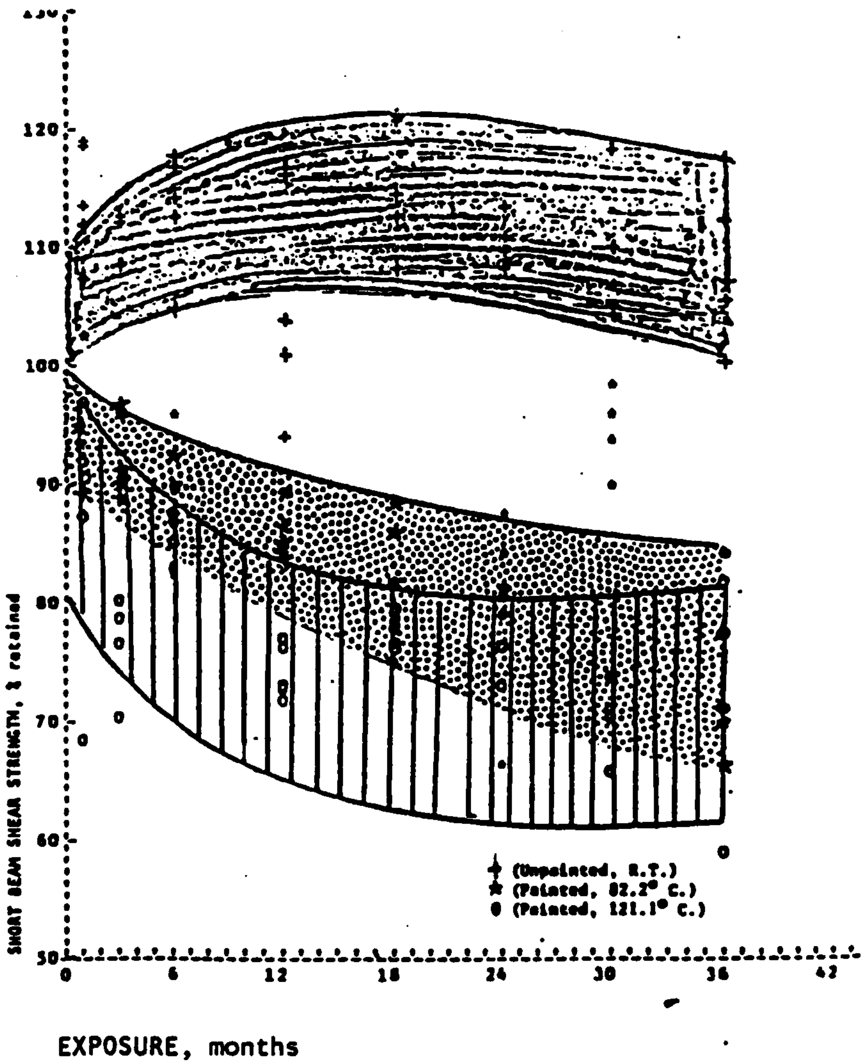

Figure 2. 400 Series, 10 Ply (± 45 90) Warminster, % Retained Short Beam Shear Strength

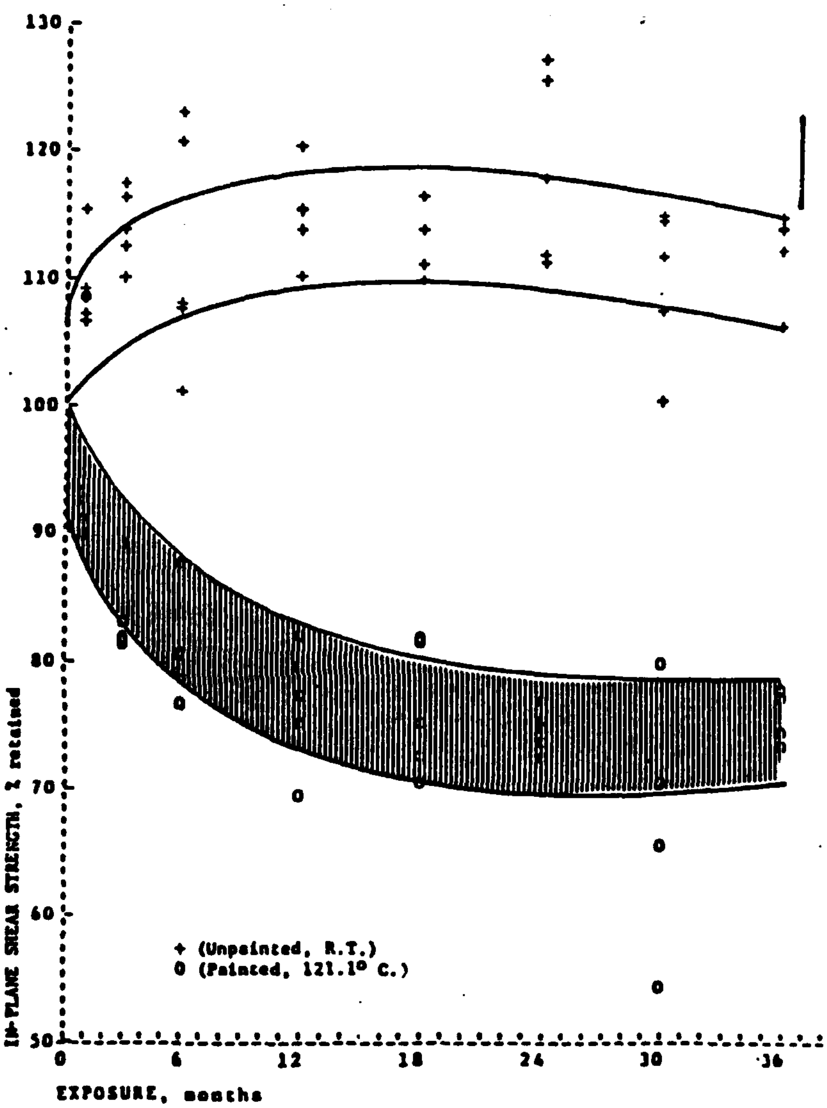

Figure 3. 900 Series, 8 Ply (± 45) Panama, % Retained In-Plane Shear Strength

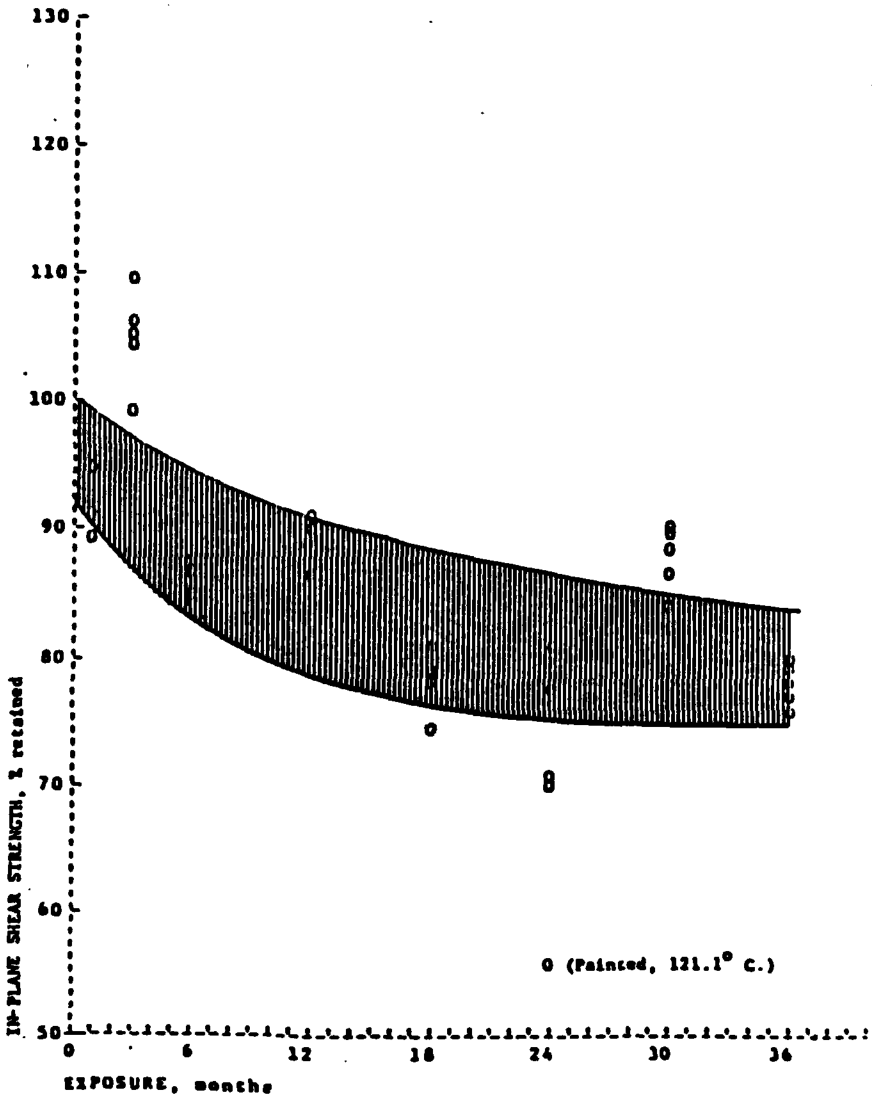

Figure 4. 900 Series, 8 Ply (± 45) Warminster, % Retained In-Plane Shear Strength

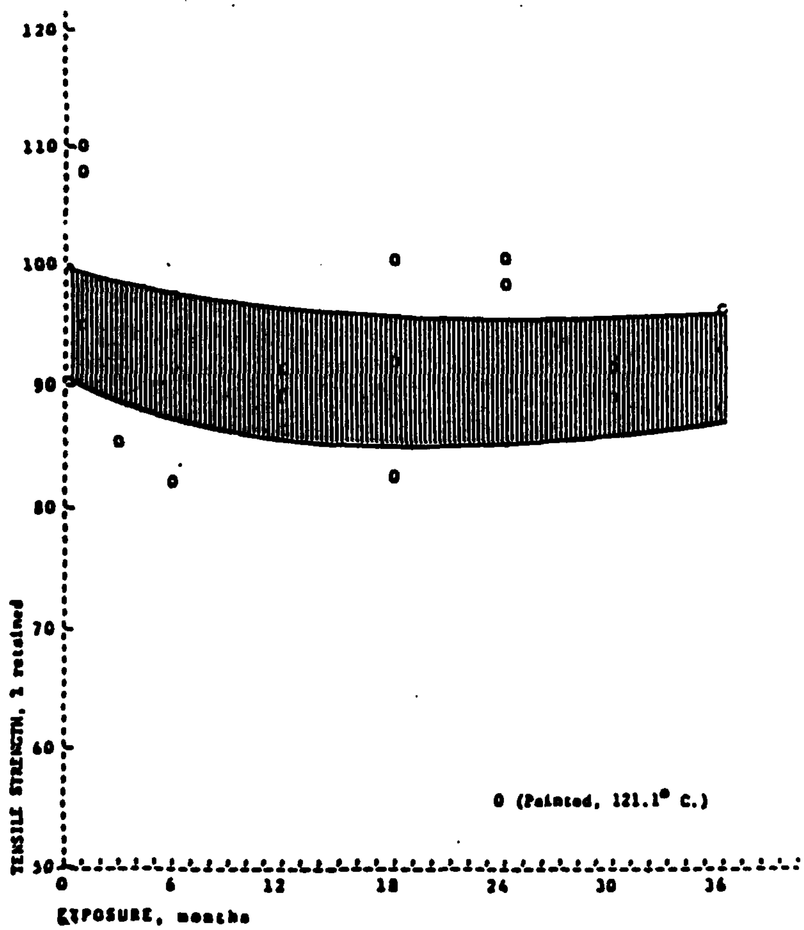

Figure 5. 900 Series, 16 Ply (0 ± 45 90) Panama, % Retained Tensile Strength

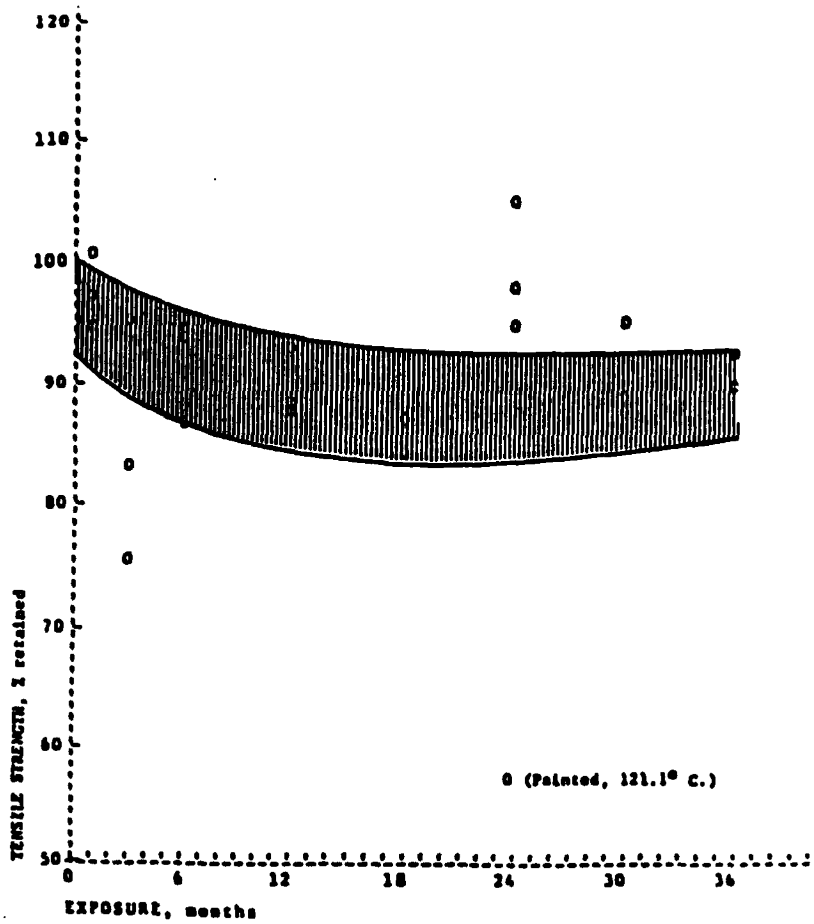

Figure 6. 900 Series, 16 Ply (0 ± 45 90) Warminster, % Retained Tensile Strength

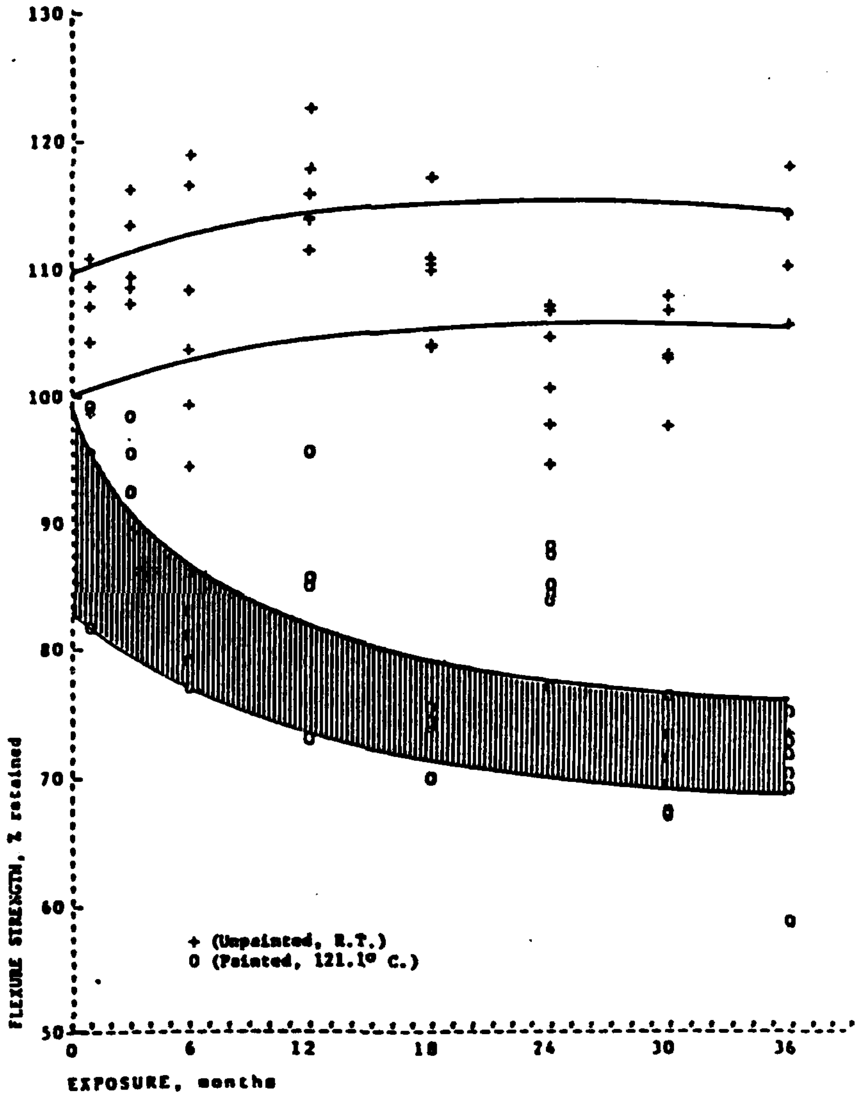

Figure 7. 900 Series, 16 Ply (0 ± 45 90) Panama, % Retained Flexure Strength

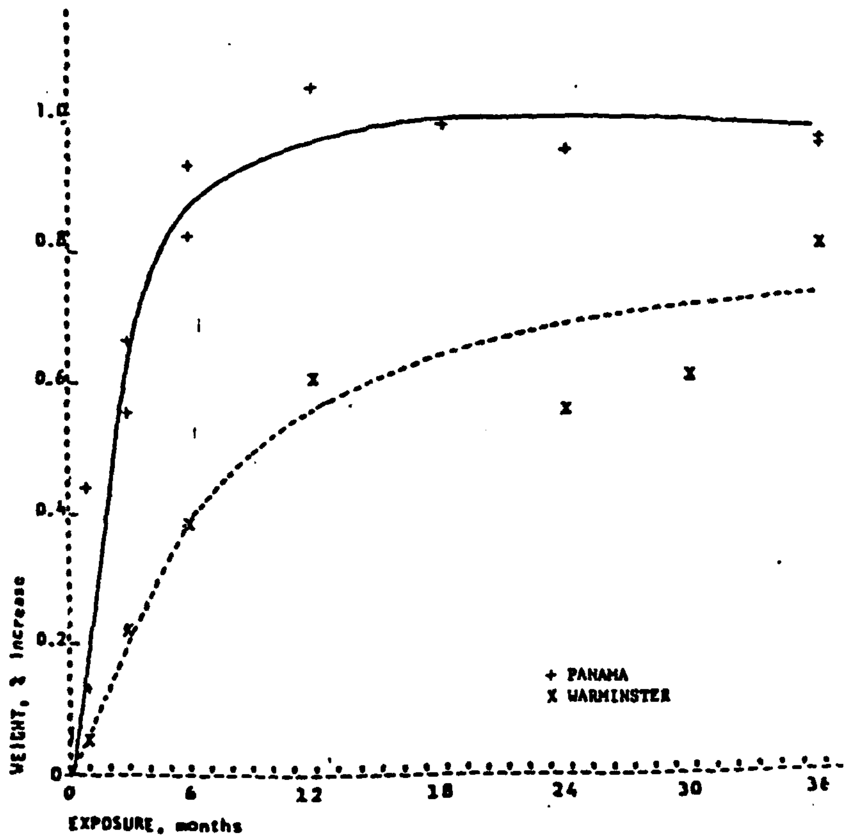

Figure 8. 900 Series, 16 Ply (0 ± 45 90) Panama (+) and Warminster (X) % Weight Increase, Painted Panels

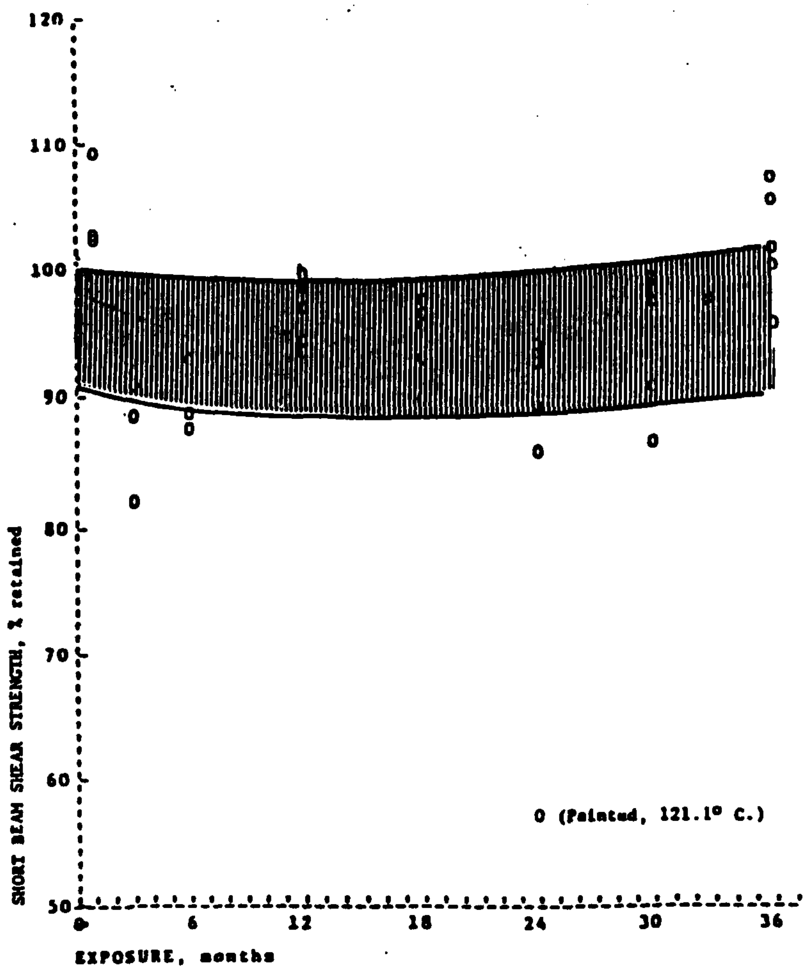

Figure 9. 800 Series, 16 Ply (0 ± 45 90) Warminster,% Retained Shear Strength

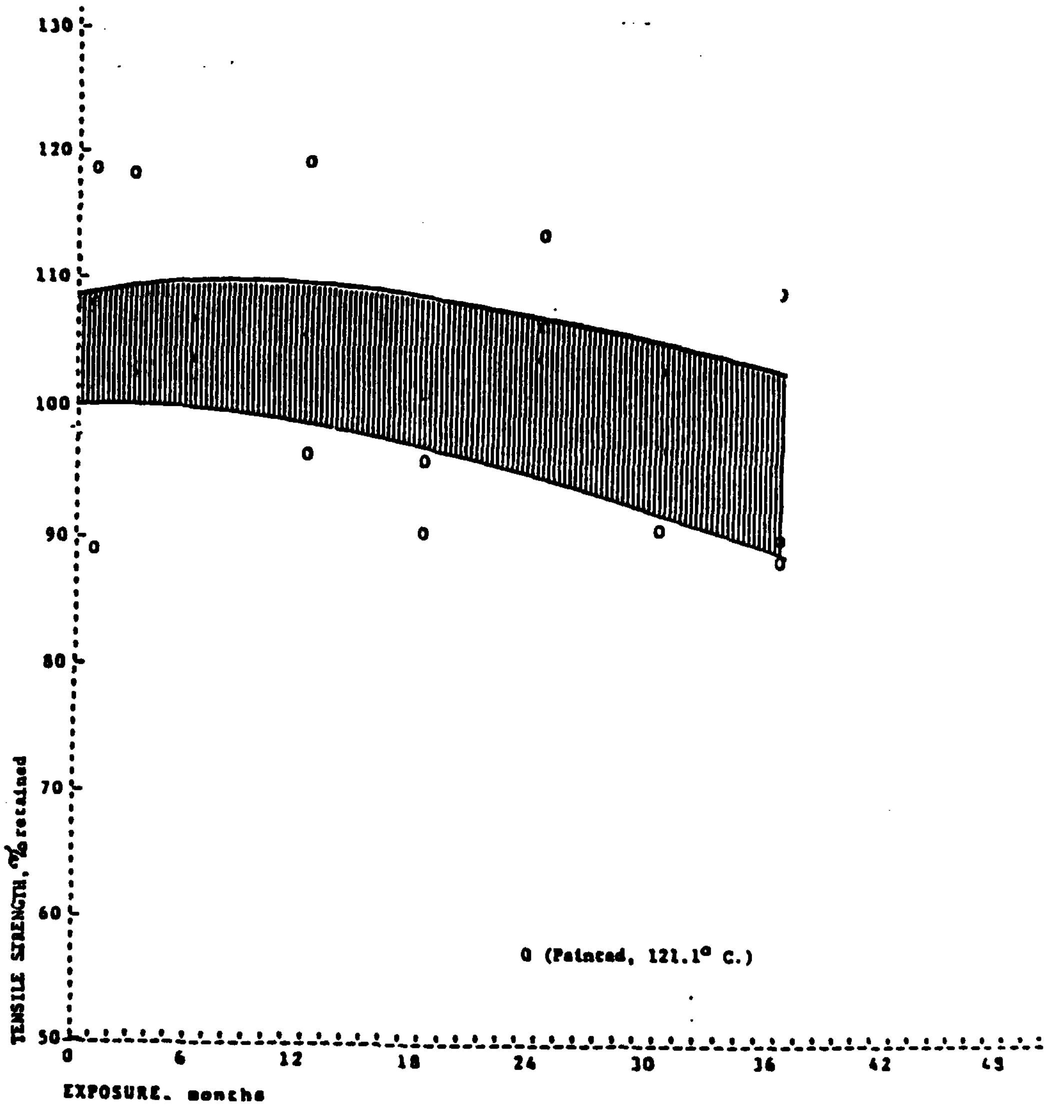

Figure 10. 800 Series, 16 Ply (0 ± 45 90) Warminster, % Retained Tensile Strength

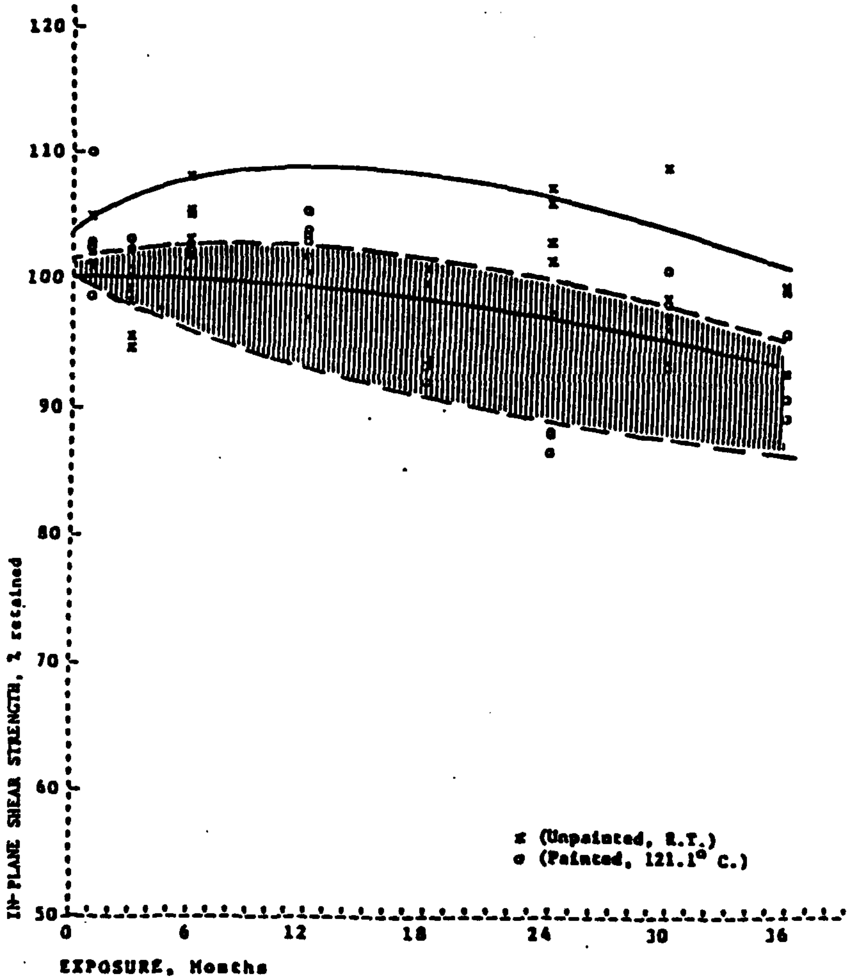

Figure 11. 1000 Series, 8 Ply (± 45) Panama, % Retained In-Plane Shear Strength

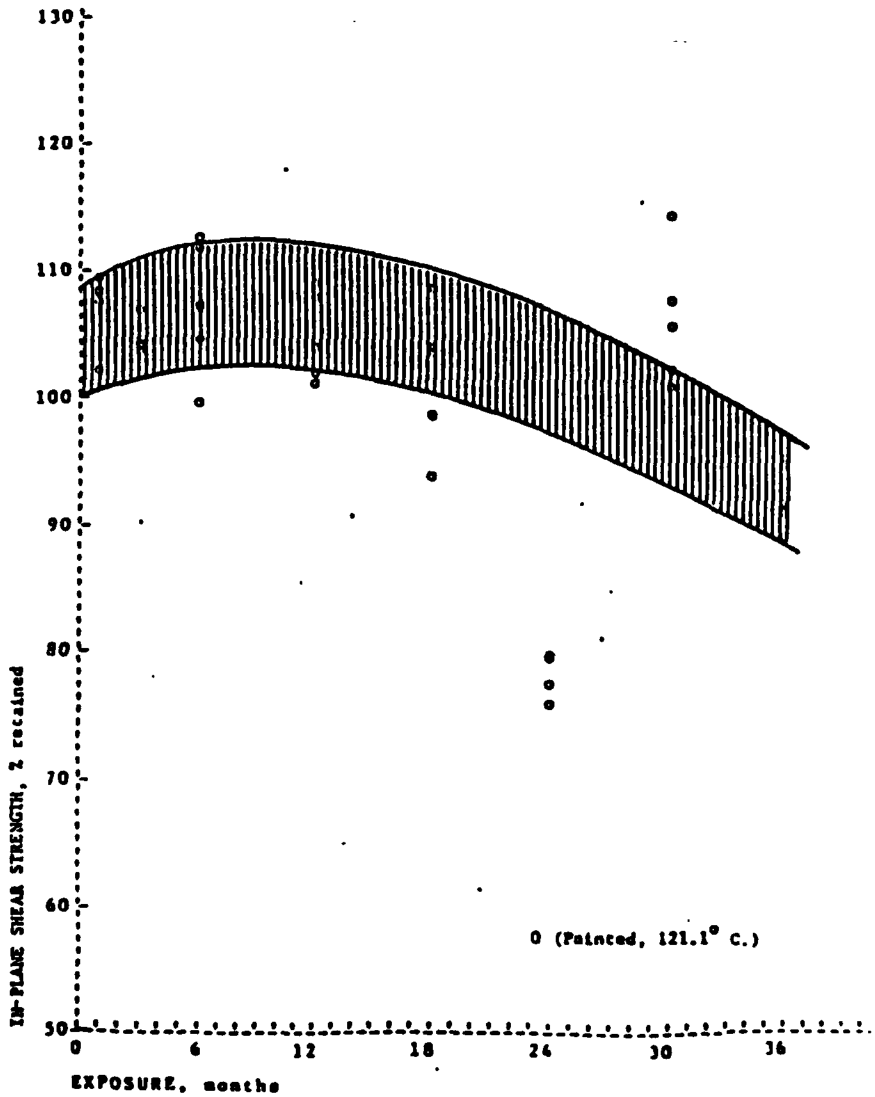

Figure 12. 1000 Series, 8 Ply ($\pm$ 45) Warminster, % Retained In-Plane Shear Strength

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